

PATENT SPECIFICATION

(11) 1 392 087

1 392 087

- (21) Application No. 14965/72 (22) Filed 30 March 1972
 (31) Convention Application No. 130 192 (32) Filed 1 April 1971 in (19)
 (33) United States of America (US)
 (44) Complete Specification published 23 April 1975
 (51) INT CL² D06M 15/28; B29H 9/04; B32B 25/10; D07B 1/02
 (52) Index at acceptance
 D1T 1B 1H 1M 1Q
 D1P AX B3 C1B C2A12A3 C2A12A9 C2A12B4 C2A12B5
 C2C1 C2C3 C2C5 C2C6 C2C9 C2CX
 F4G X6



(54) IMPROVEMENTS IN OR RELATING TO GLASS FIBER BUNDLES

(71) We, PPG INDUSTRIES, INC., a Corporation organised under the laws of the State of Pennsylvania, United States of America, of One Gateway Center, Pittsburgh, State of Pennsylvania, 15222, United States of America, (assignee of Norman Gene Bartrug), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to coated glass fiber bundles suitable for rubber reinforcement and methods for preparing same.

It has long been recognized that glass fiber material should make an ideal reinforcement for rubber products, such as automobile tires (U.S. Patent No. 2,184,326), and other elastomeric products. In preparing glass fiber materials for such applications, individual glass fibers and groups of glass fibers in the form of strands, roving, and fabric are coated with a rubber adhesive to aid in bonding of the glass to the elastomeric material to be reinforced. The rubber adhesive comprises a resin and an elastomeric latex material to link between the glass and the main body of material being reinforced. It is well known that, despite its great strength, glass cannot successfully strengthen materials in which it is embedded unless stresses imposed upon the weaker host material are transferred to the glass. This requires bonding between the reinforced material and the glass which can support shear stress without slippage and requires that continuity of the glass be maintained. In the past the possibility of interfilamentary abrasion and wear to glass fibers during flexure of reinforced rubber has prevented full exploitation of glass fiber cord as a belting material for automobile tires.

It has long been an objective to use glass fiber as reinforcement in a manner which would take full advantage of the strength and strength to weight ratio of glass. Some workers have proposed increasing the thickness of adhesive coating surrounding the bundle of glass fibers making up a reinforcing cord. By a two step processing technique it has been proposed that glass fibers may be coated with an elastomeric latex coating, then the coated fibers processed into strands, yarns, cords, fabrics or other bundle forms and thereafter impregnated to obtain a product with coating throughout. Such prior art methods do not generally provide a product with an interconnecting phase of coating throughout to join and strengthen the bundle. In general such products do not obtain complete fiber encapsulation and the methods are characterized by difficult handling of stiff, precoated fibers during bundle formation.

It has been common practice in the production of fiber glass reinforcing cords and other bundle forms to coat individual fibers with a sizing, then form the fibers into bundle form and coat the bundle by dipping or otherwise contacting a coating material which is compatible with and adheres to the ultimate material to be reinforced.

Known methods do not prepare the glass fiber bundles in a manner which will exploit to maximum advantage the strength of glass itself as a reinforcing material for elastomeric materials. Until now there has been no definitive understanding of what kind of fiber glass bundle could perform in superior fashion to those already available. By practice of the present invention there may be provided a superior reinforcing material comprising a bundle of glass fibers which is characterized as resistant to abrasion of glass against glass,

cooperative with host materials being reinforced to transmit stresses to the glass itself and suited to impart strength to a host reinforced material even after repeated flexure.

According to the present invention there is provided a glass fiber bundle of a fabric formed of a plurality of said bundles, suitable for reinforcing a host elastomeric material, said or each bundle comprising a plurality of coated glass filaments, the coating on said glass filaments being formed from an elastomeric latex-containing coating liquid, said coating having an effective mean film thickness (as herein defined) on the glass filaments of at least nine times the mean particle size of the elastomeric latex of the coating liquid whereby the individual filaments are characterized by substantially complete film encapsulation, with the coating comprising at least 26 percent by weight of the glass within the or each bundle, and said coating forming a substantially continuous interconnecting phase throughout the or each bundle.

According to the present invention there is also provided a method of impregnating a glass fiber bundle said bundle comprising a plurality of glass filaments, or a fabric formed of a plurality of said bundles, with an elastomer containing coating to effectively encapsulate each filament in the or each bundle and provide a substantially interconnecting coating throughout the or each bundle comprising:

a) contacting a sized glass fiber bundle or a fabric formed of a plurality of said sized glass fiber bundles with a coating liquid comprising at least 28 percent by weight solids in water, said solids comprising on a weight percent of total solids basis 8 to 15 percent phenolic polymer and 80 to 87 percent elastomeric latex;

b) drying the coated bundle or fabric simultaneously removing water from within the bundle or fabric and from the surface of the bundle or fabric leaving solids from the coating liquid throughout the bundle or fabric in an amount of at least 26 percent by weight of the glass in the bundle or fabric, said coating having an effective mean film thickness (as herein defined) on the glass filaments of at least nine times the mean particle size of the elastomeric latex; and

c) curing the coating throughout the glass fiber bundle or fabric.

The glass fiber bundles of the present invention may be effectively used to reinforce elastomeric compositions which are adherent to the coating.

Glass fiber bundles in the form of strands, yarns, and cords and fabrics formed from fiber bundles are impregnated with coating liquids containing elastomeric latices (both natural and synthetic latices may be used) such that each fiber is substantially encapsulated with

coating and a continuous interconnecting body of coating exists from the interior of each bundle, adjacent each fiber, and outward in surrounding relation to the entire bundle. The coating interacts with and adheres to a host material being reinforced such as a rubber. Useful elastomeric latices include styrene-butadiene-vinylpyridine terpolymers, neoprene, isoprene, butyl rubber, butadiene-styrene copolymers, acrylonitrile-butadiene-vinylpyridine terpolymers, and mixtures thereof.

Preferably included in the coating composition are phenolic polymeric materials which interact with the selected latex bond, the host material to the glass, or to a coupling agent bonded to the glass. Typical phenolic polymers which are advantageously present in the interfilamentary coated fiber bundles of this invention include novolak resorcinol-formaldehyde polymers, phenolformaldehyde and mixtures thereof. Rubber adhesive systems, generally known, which are useful in the practice of this invention include those disclosed in U.S. Patents No. 2,691,614, No. 2,817,616 and No. 2,822,311.

Host materials suitable for reinforcement by the interfilamentary coated fiber bundles of this invention include natural rubber as that derived from the Hevea tree and synthetic rubbers, such as styrene-butadiene rubber, nitrile rubber, butyl rubber, neoprene, polysulfide rubbers, polyurethane rubber and stereo-regular polymers, such as polybutadiene (including both cis- and trans-forms), polyisoprene and mixtures thereof.

Preferably included on each glass fiber is a coupling agent such as a silicon-containing organic compound which establishes a bond with the glass through the silicon and a bond with the coating composition through the organic radicals attached to the silicon. Typically useful reactants which may be applied to the glass and yield products which function as coupling agents are organo silanes, such as gamma-aminopropyltriethoxy silane, N-bis (beta-hydroxyethyl) gamma-aminopropyltriethoxy-silane, N-(trimethoxysilylpropyl) ethylene diamine, $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{COOCH}_3$, gamma-glycidoxypolytrimethoxy silane, vinyltriethoxy silane, gamma methacryloxypropyltrimethoxy silane, vinyltriethoxy silane, vinyltris(beta-methoxyethoxy)-silane, and beta(3,4-epoxycyclohexyl) ethyltrimethoxy silane. Typical of the sizes which may be applied to the glass fibers of this invention are the sizes disclosed in U.S. Patents No. 3,437,517 and No. 3,459,585.

Usually in the application of the size to bare glass other components will be present in the sizing mixtures. Residue of materials added to ease processing such as textile lubricants, emulsifiers, wetting agents, and catalysts remain in the finished interfilamentary coated glass fiber bundles. Further, one or more of

the above mentioned other components is usually included in the coating composition. A description of the materials added to aid in processing will serve to identify constituents which may be found in the final article and will serve to describe at least some typical methods for producing an interfilamentary coated glass fiber bundle suited for rubber reinforcement. Typical materials which may be present include the following: vegetable oil, amylose starch, amylopectine starch, fatty acid amides, ammonia-soluble carboxyl containing polymers, such as acrylic interpolymers and carboxylated elastomers, cellosolves ("Cello-solve" is a registered Trade Mark), alkali metal salts, oxy- (i.e. phenoxy)-polyalcohols, imidazoline reaction products, ethylene oxide derivatives of sorbitol esters, and polyethylene glycol.

Typically, the glass will be coated using aqueous mixtures containing the coating materials. The glass may be sized and coated with a single mixture, or the glass may be sized by any conventional or known sizing method using commonly known materials than later coated as a fiber bundle to produce the article here disclosed. Also, treatment may include heat cleaning or other removal of lubricants, starches, and oil after sizing and before coating filament bundles to produce the articles here disclosed.

It will be understood that organic solvents may be used, provided that they do not adversely affect the particle size of the latex. The below indicated particle sizes are to be considered applicable for purposes of this invention even in organic solvent systems.

A preferred method of producing the interfilamentary coated glass fiber bundles of this invention is to contact a continuous bundle, as for instance a cord, which has previously been sized, in a highly concentrated latex aqueous coating bath additionally containing a resin and a suitable pH buffer, to then dry the coating within and about the bundle and then cure the coating residing within and about the bundle and in intimate contact with each sized glass fiber.

A preferred method of making glass fiber bundles which may be used in practice of the present invention is based upon the method described in U.S. Patent No. 3,619,252 and U.K. Patent No. 1,204,343.

Briefly, the teaching of U.S. Patent No. 3,619,252 and U.K. Patent No. 1,204,343 comprehends combining in parallel relation and passing through a guide and in tangential contact across motor driven rollers a plurality of glass fiber strands, each having a slight twist to provide strand integrity, which have previously been sized. The rollers are partially immersed in an aqueous rubber emulsion dip and pick up this coating material when rotated. The coating, which is picked up is brought into contact with the glass fiber

strands, coating and impregnating the combined bundle of strands. Relaxation of tension in the combined bundle of strands opens the spacing between fibers and between strands enhancing impregnation of the dip into the bundle. The total impregnation is limited by the volume available between the fibers and strands and by the volume of coating solids in the total dip volume which fills the voids in the bundle. High solids concentration in the dip is required to obtain full impregnation with rubber adhesive and not merely water. The resin and latex fraction of the aqueous dip will exceed 28 percent by weight and preferably be between 30 and 40 percent by weight.

After contacting the fiber glass bundle with the dip for sufficient time to fully impregnate the bundle with the water and solids-containing dip the bundle is passed through a dielectric heater or drying oven. The drying oven is so designed and operated that water is removed rapidly from inside the bundle, as well as from the surface of the bundle, without substantial migration of the solids from the interior to the surface and without excessive blistering.

The dried glass fiber bundle is then subjected to heat to cure the rubber adhesive coating throughout the bundle.

A second method for making the glass fiber bundles of this invention is based upon the method described in U.S. Patent No. 3,718,448.

Upon forming, individual glass fibers are drawn over a roller coating applicator, such as described in U.S. Patent No. 2,873,718. An aqueous rubber adhesive dip having a high solids content, above 24 percent by weight phenolic polymer and elastomeric latex, is applied to the fibers passing over the roller.

The coated fibers are brought together into strands and are dried. Drying is accomplished by passing the strands through a dielectric oven, a hot gas or convection oven, or an infrared radiant heating chamber. Strands of glass fibers are brought together into cords or rovings and further heated to cure the resin and latex and bond strands together in the bundle. Thereafter, the composite glass fiber bundle may be further impregnated with coating.

Until now workers in the art of preparing glass fibers for use as reinforcement for rubber have directed efforts toward finding ways of obtaining improved properties, particularly improved flex strength, toward finding coating materials of improved properties, increasing the coating thickness about the fiber bundles themselves and coating fibers before bundling into cords. Improvements have been made, but a full understanding of what factors must be influenced or controlled to develop desired reinforcement characteristics has been lacking, thus preventing the exploitation

of the full potential of glass fiber as a rubber reinforcing material.

It has now been discovered that by dip impregnating of sized glass fiber bundles of "G" fibers with coating mixtures containing at least 28 percent by weight solids (based on the mixture or solution weight) comprising elastomer latices and phenolic polymers an impregnated glass fiber bundle is produced which is characterized as having a minimum individual filament coating of at least nine times the mean particle diameter of the latex and a substantially uniform and continuous interconnecting coating phase of the latex in the interfilamentary spaces and surrounding the bundle. Of the solids in a coating mixture, phenolic polymer content may vary from 8 to 15 percent by weight and latex from 80 to 87 percent by weight with the remainder active or inert material which does not interfere with the adhesive function of the resin and latex.

It has been found that such interfilamentary coated glass fiber bundles when used to reinforce rubber exhibit superior adhesion to the rubber and the resulting reinforced products possess superior tensile strength especially after repeated flexure. The articles of this invention, insofar as they are charac-

terized by an effective film thickness on individual filaments, represent a substantial departure from prior art impregnated fiber bundles and are defined in terms of this physical characteristic which has been found to be a most meaningful parameter in the evaluation of glass fiber bundles for rubber reinforcement.

In order to ensure a minimum film coverage on all filaments it has been found that the average or mean film thickness should exceed at least nine times the mean particle size of the latex starting material and preferably exceed ten times its mean particle size. A preferred minimum mean film thickness is 7000 angstroms (Å), and, when the latex used is styrene-butadiene-vinylpyridine, a minimum mean film thickness of 9000 angstroms is preferred.

The effective mean film thickness may be calculated as a function of the weight gain of a fiber bundle due to coating pickup. The calculation is based on the assumption that filaments are in a hexagonal close packing configuration to minimize void volume, and this is to be consistently applied to any bundles under comparison.

The general relationship exists:

$$\frac{D_2^2}{D_1^2} = \frac{1 + \left(\frac{\alpha \text{ glass}}{\alpha \text{ coating}} \right) \left(\frac{\text{weight percent coating}}{100} \right)}{1 + (1.1) \left(0.093 + \frac{\text{percent skin}}{100} \right)}$$

where

α = specific gravity

0.093 = void fraction

percent skin = fraction of bundle volume due to coating deposited around the perimeter of the outermost fibers determined by observing a 300× to 1500× magnified photograph of bundle cross-section and defining a perimeter as the shortest continuous perimeter about all the fibers and within the coating surface

D_1 = filament diameter (mean)

D_2 = filament diameter including effective films (mean).

Weight percent coating as a percent by weight of the bare glass is determined from a loss on ignition. The determined coating weight includes size which is normally 0.5 to 1.5 percent and is ignored for these calculations. Except for diameters, the terms are dimensionless and the diameters may be expressed in any convenient units.

Effective film thickness is

$$t = \frac{D_2 - D_1}{2}$$

In the case of products which have had coating applied directly to filaments, as by direct coating strands prior to gathering into strands and cords, it has generally been observed that voids between small groupings of filaments remain unfilled. If there has been no subsequent bundle coating and the voids remain, there is no skin effect, and the following relationship has been found to exist.

$$\frac{D_2^2}{D_1^2} = 1 + \left(\frac{\alpha \text{ glass}}{\alpha \text{ coating}} \right) \left(\frac{\text{weight percent coating}}{100 - \text{weight percent coating}} \right)$$

$$t = \frac{D_2 - D_1}{2}$$

The terms are those earlier defined. If there has been a subsequent overcoat the relationship immediately above holds with the weight percent coating diminished by the amount of coating in the skin around the full bundle perimeter.

The calculated effective film thickness is to be compared with the mean particle diameter of the particular latex employed to determine if effective encapsulation exists. Typically useful latices are listed below accompanied by their effective mean particle diameters as applied from aqueous mixtures without consideration of cross-linking in-situ within a glass fiber bundle. These are appropriate diameters for purposes of comparison with coating film thicknesses determined for glass filaments in a glass fiber bundle. The mean particle size of latex in a coating is the average of all latices in the coating.

	LATEX	MEAN PARTICLE DIAMETER
25	Styrene-butadiene-vinylpyridine	800—1000 Å
	Neoprene	800—1600
	Isoprene	2000—5000
	Butyl rubber	2000—5000
30	Butadiene-styrene copolymer	1200—1500
	Acrylo-nitrile-butadiene-vinylpyridine	1000—2000

These above materials are examples of suitable materials having adhesive quality and particle sizes ranging from 2000 to 10,000 angstroms, preferably 500 to 5000 angstroms, which may be used in this invention.

It has been further found necessary to employ a coating comprising at least 26 percent by weight of the bare glass to ensure the complete encapsulation of the glass filaments. Measurement of total pickup as a loss on ignition is easily and quickly done by production personnel, and the film thickness, when checked intermittently, may be used to confirm process control.

A lower limit of 26 weight percent pickup of coating is sufficient to ensure protection of "G" fibers (38×10^{-5} inch diameter) in currently common tire reinforcing cord. Cord made of "K" fibers (52×10^{-5} inch diameter) may be protected by 18 weight percent coating pickup, and 14 weight percent coating pickup is adequate to protect "P" fibers (72×10^{-5} inch diameter). In each instance the mean coating film diameter is at least nine times the mean particle size of the latex.

The invention will be illustrated with reference to the accompanying drawings, in which:—

Figs. 1A, 1B and 1C are cross-section

views of the glass fiber bundles of this invention,

Figs. 2A, 2B and 2C are cross-section views of prior art glass fiber bundles.

FIG. 3 is a diagrammatic representation of a typical flow process that may be employed in preparing the glass fiber bundles of this invention, and

FIG. 4 is a diagrammatic representation of a high frequency dielectric heating apparatus that may be employed in preparing the glass fiber bundles of this invention.

FIG. 1A illustrates an idealized cross-section of a G—75 5/0 cord, 5 of five strands, 4 impregnated with a rubber adhesive coating according to this invention. FIGS. 1B and 1C are scale reproductions of photo enlargements of cross-sections of a strand 4 of Figure 1A. FIG. 1B shows a major portion of a strand 4 enlarged 300 times in the cord 5 with the cord surface appearing. FIG. 1C, enlarged 700 times, illustrates the complete uniformity of coating throughout the bundle and clearly shows the separation of glass fibers by coating.

FIG. 2A illustrates an idealized cross-section of a G—75 5/0 cord, 5 of five strands, 4. FIGS. 2B and 2C are scale reproductions of photo enlargements of cross-sections of a strand 4 of Fig. 2A. FIG. 2B, enlarged 300 times shows the major portion of a strand, 4, in the cord, 5, with the cord surface appearing. FIG. 2C, enlarged 700 times, illustrates the discontinuity of coating throughout and shows regions where adjacent glass fibers are in contact unseparated by coating.

A method of producing the coated cord of the invention will be described with reference to Figs. 3 and 4. Fig. 3 shows a creel 1 having mounted thereon a plurality of bobbins 3 containing glass fiber strand 5. The filaments forming the glass fiber strands 5 are coated with a sizing material comprising a lubricant, binder and coupling agent before they are gathered to form the strands. Furthermore, as is conventional, each of the glass fiber strands 5 has imparted therein a 1.4 turns per inch twist to provide strand integrity and resistance to fuzzing during initial handling or processing prior to being coated and impregnated with elastomeric material.

The strands 5 are combined in parallel relation and passed through a ceramic guide 7, in tangential contact across motor driven rotating rollers or dip applicators 9, to a motor driven rotating wiper roller or pulley 11. The rollers or dip applicators 9 are partially immersed in an aqueous rubber dip or emulsion (i.e. coating mixture) 13 contained within vessels or tanks 15. The dip applicators 9 are driven counter to the direction of travel of the strand 5 to improve the coating of the filaments thereby improving the impregnation of the strand 5. The pickup of rubber dip 13 by the applicators 9 and strand 5 is more

than sufficient to coat and impregnate the strands with the desired (i.e. at least 26% by weight of the glass within the bundle and the rubber dip) final amount of rubber dip or adhesive material solids. The wiper roller or pulley 11 is driven with the direction of travel of the strand 5 and serves to change the direction of the strand with care to avoid removing rubber dip or adhesive material 13, except in excess of that required to obtain the beneficial effects of coating.

From the wiper roller or pulley 11, the coated, impregnated strands are passed vertically through a dielectric heater or drying oven 17, wherein certain undesirable volatile constituents of the rubber dip 13 are driven off and removed from the dielectric oven 17 by means of a blower 19. A suction device (not shown) could be used in lieu of or in addition to the blower 19 and would preferably be located adjacent the upper or exit end of vertically arranged dielectric oven 17. The construction of a typical dielectric heating or drying oven, suitable for use with the present invention, is shown more fully in FIG. 4.

Referring to FIG. 4, there is shown a diagrammatic representation of dielectric heater 17 comprising a vertically arranged series of spaced electrodes 25 electrically connected to a suitable power source (not shown) to produce an alternating, high frequency electrical field 27 between successive oppositely charged electrodes. As the strands 5, coated and im-

pregnated with aqueous rubber dip 13, traverse across but not contacting the electrodes 25 and through fields 27, the liquid component of the dip, water which has a higher dielectric constant than the solid component, is electrically activated to produce a uniform heating action throughout dip material 13. The rate and amount of electrical activation or dielectric heating is controlled to the extent of removing or volatilizing substantially all of the liquid component of the aqueous dip material while leaving the solid component substantially unaffected. The coated and impregnated strands 5, as they leave dielectric heater 17, are free of bubbles and sufficiently dry and free of tack for the purpose of further processing the strand over rolls, or pulleys without fear of stripping off coating material and/or depositing coating material on supporting and conveying elements.

Thereafter, the coated strands pass upwardly and then traverse through a hot gas oven 21 or other suitable heating device to cure or react the solid component of the adhesive 13, as will be explained more fully hereinafter. Following attainment of the desired degree of cure, the adhesive coated glass fiber strands are removed from the curing oven 21 and collected on a suitable take-up device 23.

A suitable coating mixture for use in the present invention is one having the following composition:

INGREDIENT Functional Description (Material)	RANGE Parts by weight:	PREFERRED Parts by weight
Vehicle — Deionized Water	89.7 — 139.7	111.7
pH Control — Ammonium Hydroxide (28% aqueous solution)	0.4 — 2.0	0.5
Adhesive —		
Resin — Novolak Resin (75% solids)	10.7 — 26.7	16.4
— Formaldehyde (37% aqueous solution)	2.7 — 10.8	7.4
Latex — Styrene-butadiene-vinylpyridine (15:70:15) (41% solids)	146 — 244	244.0
— Styrene-butadiene rubber (41% solids)	0 — 97.5	0

On a solids basis the novolak comprises 11.6 to 12.2 percent by weight, the formaldehyde 1.4 to 2.5 percent by weight, and the

combined latex 85 to 87 percent by weight, the styrene-butadiene-vinylpyridine being from 61 to 87 percent by weight and the styrene-

butadiene rubber being 0 to 25 percent by weight. Solids content of the preferred coating dips shown above range from 28 percent to 31.5 percent by weight of the liquids with the preferred composition 30 percent by weight solids.

In coating compositions having greater solids content, as for instance above 28 weight percent solids, the use of a novolak resin is preferred to use of a resorcinol-formaldehyde system. Less precipitation or "throwing out" occurs from large batches of coating solution when a novolak resin is used.

The coating liquid (an emulsion) is prepared by adding the water to a premix tank followed by the addition of ammonium hydroxide while stirring and then adding the novolak to this mixture while stirring, continuing stirring until complete solution. The particular novolak used in the example described was that marketed by Koppers Company under their trade name Penacolite R-2170. The styrene-butadiene-vinylpyridine is added to a batch tank and to it is added the styrene-butadiene rubber with stirring followed by continued stirring for about five minutes. The particular commercial latices used in the examples which follow were, unless otherwise indicated, a styrene-butadiene-vinylpyridine sold by General Tire & Rubber Company and designated Gentac ("Gentac" is a registered Trade Mark) and a styrene-butadiene rubber sold by General Tire & Rubber Company under the designation Genflo. The premix is then added to the batch tank with stirring which is continued for five minutes after addition. The formaldehyde is then added to the mixture and the mixture stirred for ten minutes. The coating mixture is allowed to age for at least about six hours before use.

Glass fiber cord (G-75 5/0, filament count 2000 i.e. cord from filaments designated as G-fibers which have an average diameter 3.6×10^{-4} inches, 7,500 yards of which constitutes a pound, the cord having 5 strands) which has been sized during forming according to the conventional methods described in U.S. Patent No. 2,728,972 is coated with the above coating. The sizing present on the glass may be any typical size containing a silane coupling agent as described above. A preferred size and that used in the examples, unless otherwise indicated, is the size described in U.S. Patent No. 3,655,353.

The resulting coated yarn has an excellent appearance indicating apparent uniform coating distribution throughout. The yarn is freely flexible and when bonded in rubber is found to adhere with superior adhesion. The rubber-coated yarn combination has superior tensile strength and flex resistance when compared with other less impregnated coated yarns. A determination of effective film thickness on individual fibers based upon a measured weight percent of coating of 30 percent, a skin frac-

tion of 4 percent, an average bare glass filament diameter of 38×10^{-5} inch and a ratio of glass to coating specific gravity of 2.5 indicates a mean effective film thickness of 12,250 angstroms which being in excess of 13 times the latex particle size indicates complete filament encapsulation, the mean particle size of the styrene-butadiene-vinylpyridine being 900 angstroms. Photo-micrographs of cord cross-sections having magnifications of $300\times$ to $700\times$ confirm complete filament encapsulation and the desired minimum film thickness and indicate a substantially continuous interconnecting phase of coating throughout the bundle.

By "substantially continuous interconnecting phase of coating" it is meant that any two randomly selected glass fibers anywhere in a cord cross-section are joined by coating. When viewing an enlargement of a cross-section of the glass fiber bundles of this invention, as in FIGS. 1B and 1C, it is apparent that a path may be traced between any two fibers 2 while remaining within the indicated coating phase 6. It may be noted in FIGS. 2B and 2C, depicting prior art glass fiber bundles, that some fibers 2 are neither surrounded by coating 6 nor, connected by coating to other fibers but are bare, rubbing against other fibers in voids 8 within the bundle. While both the bundles of this invention and those of the prior art have voids 8 within the bundles, those in the bundles of this invention do not contact and do not surround fibers 2 in the bundle.

The skin of coating 9 about the complete bundle of glass fiber is observed in part in FIGS. 1B and 2B. A perimeter drawn about the outermost fibers delineates a skin of coating about the surface and observing the full surface area of a bundle permits a determination of the skin fraction as described above.

Viewing FIGS. 1C and 2C particularly points out the complete fiber encapsulation effected by developing an average or mean effective film thickness for all fibers which exceed the particle size of the latex in the coating liquid by at least nine times. FIG. 1C is from a sample of the cord in Example I, below, having an average film thickness of 12,250 angstroms; FIG. 2C is from a sample of the cord in Example I, below, having an average film thickness of only 5500 angstroms.

The following examples will illustrate in detail the nature of this invention when compared with prior coating impregnated glass fiber bundles.

EXAMPLE I.

Two coating dips were prepared, one according to the preferred embodiment described above having 30% solids and one of the same composition except for greater water content, having 22% solids (for comparative purposes). The solids in each dip were the rubber ad-

hesive components in the dip; namely, novolak, formaldehyde and latex. Two samples of glass fiber cord, G-75 5/0, were coated by contacting one sample with the 30% dip and one sample with the 22% dip. Each coated cord

was prepared by the method described above in connection with Figs. 3 and 4.

Following coating the two samples of cord were evaluated, the comparative observations being summarized in Table I:

10

TABLE 1.

	22% solids dip	30% solids dip
Cord	G-75 5/0	G-75 5/0
Yardage (yards/pound)	1282	1117
Calculated Mean Film Thickness (Å)	5500	12,250
Coating-Dip Pickup (DPU) (As weight percent of bare glass)	17.6	33.0
Twist (turns/inch)	1.4	1.4
Cord Diameter (mils)	22.6	23.4
Breaking Strength (pounds)	58.3	64.6
Tenacity (grams/denier)	8.9	9.8
Strength in Rubber (pounds)	73.5	76.7
Adhesion (pounds)		
H-pull	10	14
Strip, Room Temperature	45.5	57.0
Strip, 250°F	35.6	40.6
Scott Flex (1000 cycles)	337	822

As evidenced in the above table the coating impregnated cord having the higher mean effective film thickness and the higher dip pickup exhibits substantially greater resistance to flex wear. Rubber reinforced with the product of this invention withstands repeated flexure without failure; in this test failure did not occur after more than twice as many flex cycles as caused rubber reinforced with less completely coating impregnated cord to fail.

Flex testing is accomplished using a Scott Flexing machine and the test method of ASTM-D-430-59. Rubber stock, 60-65 mils thick is used. Cord is laced across the rubber 9 ends per 0.75 inch. Samples are cured in a press at 250 psi and 275-325°F. for about 25 minutes. After curing, samples are quick chilled in cold water. Strips, 0.75 inch wide and containing 9 cords each are cut from samples for testing. Sample strips are placed on a Scott Flex tester at room temperature using a load of 80 pounds. The strips are cycled at 250 cycles per minute until failure and total cycles to failure noted.

Typical commercial rubber compounds used

in testing are principally styrene-butadiene rubber selected to have the following properties: optimum cure at 300°F, about 30 minutes; 300 percent modulus, about 1900 pounds/square inch; tensile strength, about 2900 pounds/square inch; elongation at failure, about 430 percent; hardness, about 64; and specific gravity, about 1.13.

Adhesion of the impregnated cords to rubber is determined by the ASTM "H-Pull" test, ASTM-D-2168-62T. Rubber, as above, 50-55 mils thick, is molded with cord to form an "H" with a cord and two 1/4 inch strips of rubber and cured at 500 psi with other conditions as indicated above. After curing the samples are water chilled and cut to standard test dimensions. Before testing, samples are heated at about 250°F for 30 minutes. Samples are then attached to grips of the test machine (Instron Tester) ("Instron" is a registered Trade Mark) and subjected to pull at a cross-head speed of 4 inches per minute — testing being performed within 15 seconds after sample removal from the oven.

Strip adhesion for rubber coated glass fiber

cord is determined by the following method. A piece of 14 inch \times 8 inch rubber is secured about the 14-1/2 inch circumference drum of a lathe leaving a space between the two ends of the rubber. The rubber is brushed lightly with benzene or toluene. The drum is rotated at about 45 rpm, winding cord about the rubber with adjacent cord windings in contact with one another. Masking tape is placed across the cords along each edge of the rubber adjacent the space. The cords passing across the space are cut and the rubber and cords removed from the drum. A two inch wide strip of Holland cloth is placed over the cord along an edge. An additional piece of rubber is laid over the cloth and cord. The sample is then folded toward the face of the first rubber piece on which the cord is laid making a 7 inch by 8 inch pad. The pad is placed in a cavity brass mold, 8 inch \times 9 inch \times 1/2 inch \times 1/2 inch brass bars with a brass block insert, 7 inch \times 8-1/2 inch \times 1/2 inch which in turn is placed in a hydraulic press preheated to 300–400°F. After 5 minutes pressure is increased slowly and held until the rubber is cured.

Five test specimens are cut from the pad. Each is 5 inch \times 1 inch and contains a portion of the Holland cloth strip. An Instron test device, as used in the tests above, is set for a crosshead speed of 2 inches per minute and a gauge length of 1/2–3/4 inch. To determine adhesion of cord-to-rubber the pad is separated by removal of the Holland cloth, and the exposed cord with rubber is attached to the bottom jaw and the exposed rubber and remaining layers attached to the top jaw. The test device is operated to separate the rubber and cord to a two inch separation. The loading is noted for all specimens in this manner and the average loading reported.

The hot tests are performed on samples heated to the test temperature for 30 minutes immediately prior to testing.

EXAMPLE II.

Glass fiber cords coated as above, except

substituting an equivalent portion of resorcinol and formaldehyde (i.e. to form resin *in situ*) in the coating for the novolak resin and formaldehyde in the above example, were prepared with varying mean effective filament coating film thicknesses and varying coating pickup. The fibers of this example were sized (prior to coating with the phenolic resin and latex composition) with a size having the approximate composition which follows. The forming size used was an aqueous size having about 4.5 percent by weight solids consisting of 470–480 parts by weight condensation product of bisphenol A and epichlorohydrin, as Epon 828, 45–50 parts by weight of a polyoxyethylated vegetable oil, such as General Aniline F.L.—719, 45–50 parts by weight alkylphenoxypoly(oxyethylene) ethanol, such as Igepal CO—630, 140–150 parts by weight polyvinylpyrrolidone, 20–25 parts by weight polyethyleneglycol monolaurate, 45–55 parts by weight fatty acid amide, such as Versamide of General Mills Company, 10–15 parts by weight glacial acetic acid, 55–65 parts by weight silane coupling agent — $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{COOCH}_3$, and optionally a silicone oil defoamer 0.1–1 part by weight.

Such cords were used to reinforce the treads of tires having side-wall or carcass reinforcement of nylon (2 ply). Two plies of bias belting, having the glass fiber cords spaced 16 cords/inch, were used to reinforce the tread of tires to be tested. All tires, identical except for coated glass fiber cord in the tread, were subjected to severe road testing on a high speed track at 75 miles/hours and a rock course at 25 miles/hour. High speed running and rock course running were alternated throughout the test. After high speed running for 6720 miles and rock course running for 2880 miles all tires were cut to expose the glass cords. Table II contains a summary of this testing.

TABLE II.
TIRE TESTING.
(2 Ply Bias Belt Coated Glass Cord in Treads)
ALL CORDS
(G-75 5/0, 2.5 tpi)

Calculated Mean Film Thickness	Dip Pickup — Coating % by Weight of Bare Glass	CORD CONDITION AFTER TEST
12,250 A	30%	No Broken Cords — cords appeared as before placement in tire.
5,750 A	18%	Few cord breaks observed; traces of powdered glass spotted throughout belt area.
3,250 A	12%	Substantially more broken cords than above tire samples; powdered glass visible throughout belt area.
1,000 A	7%	Many broken cords; large patches of powdered glass obscuring any indication of cord continuity in many regions of the belt area.

The road tests of glass fiber cord reinforced rubber tires demonstrate the great utility of the present discovery. Glass fibers with assured minimum coating coverage and thus complete encapsulation as indicated by a minimum mean film thickness several times greater than the particles used in coating are apparently less subject to interfilamentary abrasion. Reduced interfilamentary abrasion is evident from the retention of cord condition during use and the lack of powdering of glass which has been adequately coated.

Although the present invention has been described with respect to specific details of certain embodiments thereof, it is not intended to limit the scope of this invention by such details, but rather the scope is to be limited only by the claims. It will, for example, be apparent to those skilled in the art that a plurality of glass fiber bundles of this invention may be gathered together to form a larger bundle and that each smaller bundle could be examined separately to determine its character. "Bundle" as used here is not confined to any particular number of glass filaments and means any assembly of glass filaments gathered in parallel relationship.

WHAT WE CLAIM IS:—

1. A glass fiber bundle or a fabric formed of a plurality of said bundles, suitable for reinforcing a host elastomeric material, said or each bundle comprising a plurality of coated glass filaments, the coating on said glass filaments being formed from an elastomeric latex-containing coating liquid, said coating having an effective mean film thickness (as herein defined) on the glass filaments of at least nine

times the mean particle size of the elastomeric latex of the coating liquid whereby the individual filaments are characterized by substantially complete film encapsulation, with the coating comprising at least 26 percent by weight of the glass within the or each bundle, and said coating forming a substantially continuous interconnecting phase throughout the or each bundle.

2. A glass fiber bundle or fabric as claimed in claim 1 wherein the elastomeric latex in the coating liquid has a mean particle size from 500 to 5000 angstroms.

3. A glass fiber bundle or fabric as claimed in claim 1 wherein the elastomeric latex in the coating liquid has a mean particle size of from 2000 to 10000 angstroms.

4. A glass fiber bundle or fabric as claimed in any one of the preceding claims wherein the elastomer phase of the latex is selected from styrene-butadiene-vinylpyridine terpolymer, neoprene, isoprene, butyl rubber, butadiene-styrene copolymers, acrylonitrile-butadiene-vinylpyridine terpolymers, and mixtures thereof and the coating further comprises phenolic polymer selected from novolak-resorcinol-formaldehyde polymers, phenol-formaldehyde and mixtures thereof.

5. A glass fiber bundle or fabric as claimed in claim 4 wherein the elastomeric latex is a mixture of styrene-butadiene-vinylpyridine and styrene-butadiene rubber and the resin is a novolak resin.

6. A glass fiber bundle or fabric as claimed in claim 5 wherein the coating comprises from 28 to 40 percent by weight of the glass within said or each bundle.

7. An article comprising an elastomeric material reinforced with a glass fiber bundle or fabric as claimed in any one of the preceding claims.

5 8. A reinforced elastomeric article as claimed in claim 7 wherein the elastomeric material is selected from natural rubber, styrene butadiene rubber, nitrile rubber, butyl rubber, neoprene, polysulfide rubbers, polyurethane rubber, polybutadiene, cis- and trans-polybutadiene and polyisoprene, and mixtures thereof.

10 9. A method of impregnating a glass fiber bundle, said bundle comprising a plurality of glass filaments, or a fabric formed of a plurality of said bundles, with an elastomer containing coating to effectively encapsulate each filament in the or each bundle and provide a substantially interconnecting coating throughout the or each bundle comprising:

15 a) contacting a sized glass fiber bundle or a fabric formed of a plurality of said sized glass fiber bundles with a coating liquid comprising at least 28 percent by weight solids in water, said solids comprising on a weight percent of total solids basis 8 to 15 percent phenolic polymer and 80 to 87 percent elastomeric latex;

20 b) drying the coated bundle or fabric simultaneously removing water from within the bundle or fabric and from the surface of the bundle or fabric leaving solids from the coating liquid throughout the bundle or fabric in

an amount of at least 26 percent by weight of the glass in the bundle or fabric, said coating having an effective mean film thickness (as herein defined) on the glass filaments of at least nine times the mean particle size of the elastomeric latex; and

c) curing the coating throughout the glass fiber bundle or fabric.

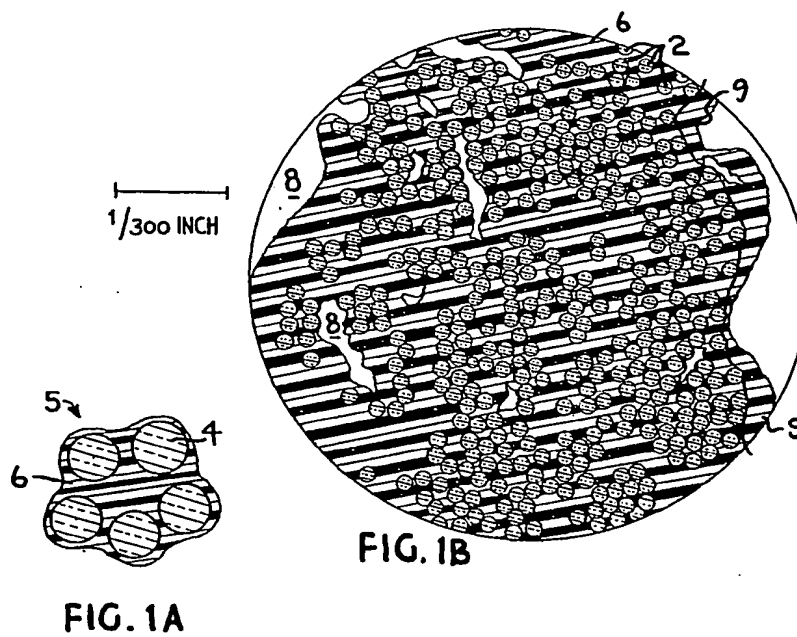
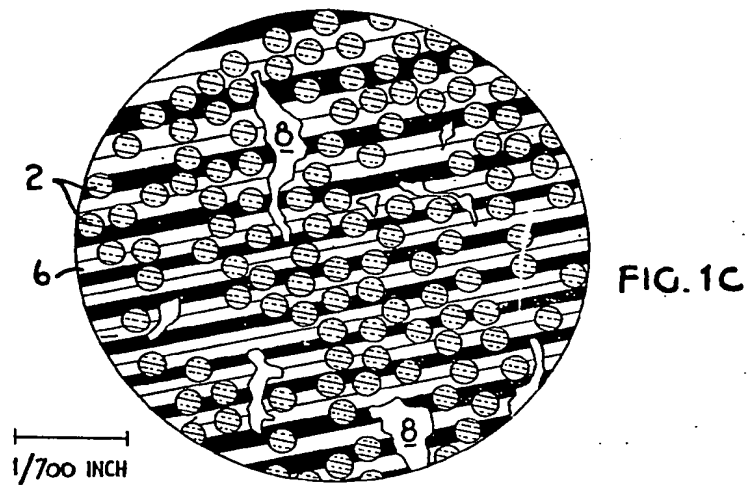
10. A method as claimed in claim 9 wherein the phenolic polymer is a novolak and the elastomeric latex is a mixture of styrene-butadiene-vinylpyridine and styrene-butadiene rubber.

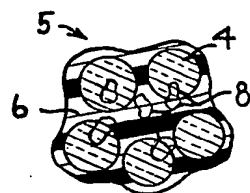
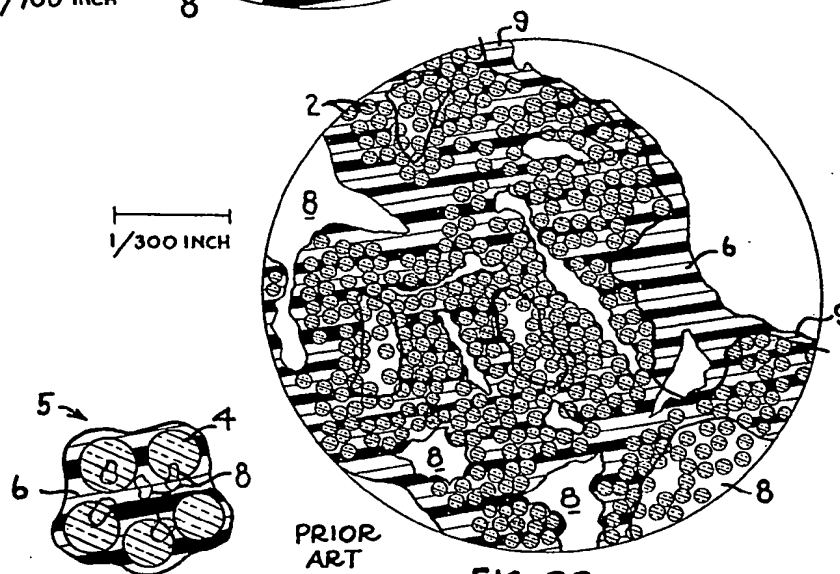
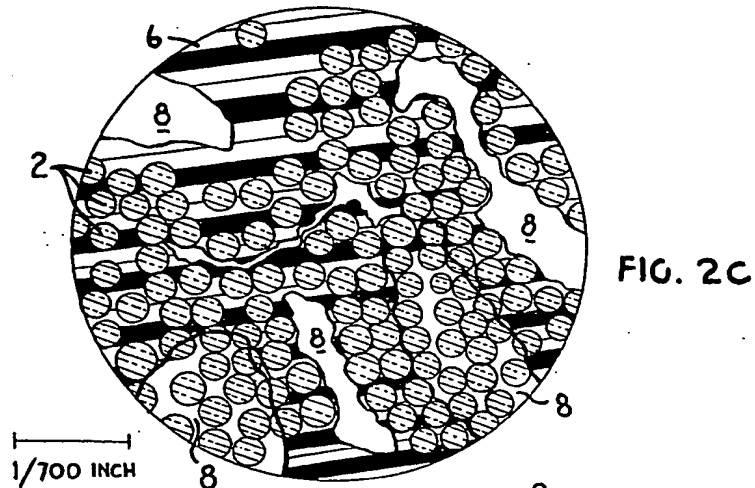
11. A method as claimed in claim 9 or 10 wherein the coating liquid comprises 89.7—139.7 parts by weight deionized water, 0.4—2.0 parts by weight 28% aqueous ammonium hydroxide, 10.7—26.7 parts by weight novolak resin (75% solids) 2.7—10.8 parts by weight formaldehyde (37% aqueous solution), 146—244 parts by weight styrene butadiene-vinylpyridine latex (15:70:15) (41% solids) and 0—97.5 parts by weight styrene-butadiene rubber (41% solids).

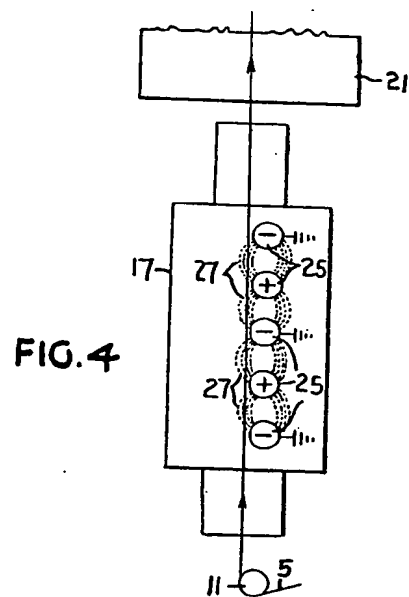
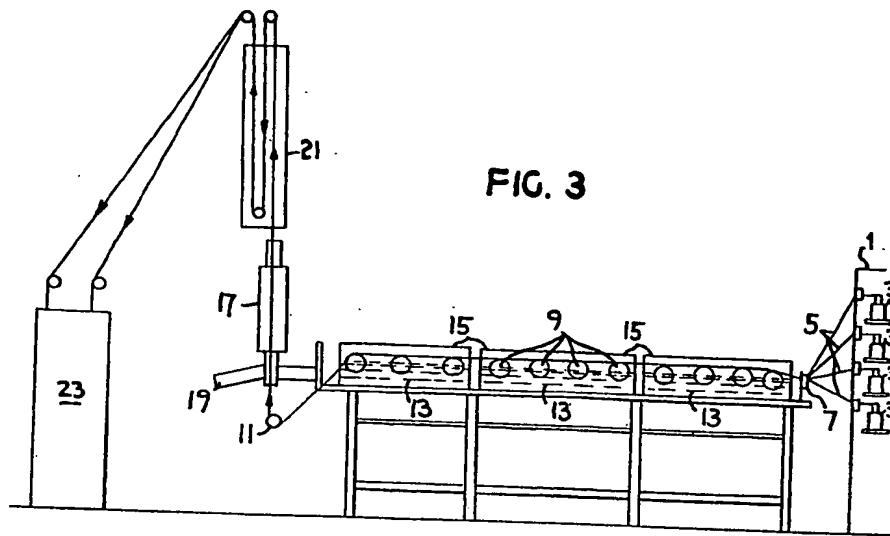
12. A glass fiber bundle or fabric as claimed in claim 1 and substantially as hereinbefore described with reference to either of the foregoing examples.

W. P. THOMPSON & CO.,
12 Church Street,
Liverpool, L1 3AB,
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.







**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.